Oral presentation

In situ study of the activation process of MOF-74 using three-dimensional electron diffraction

M. Quintelier[1], A. Hajizadeh[1], A. Zintler[1], B. Gonçalves[2], R. de Luis[2], L. Esrafili[3], C.M.L. Vande Velde[3], S. Wuttke[2,4], J. Hadermann[1]

[1]EMAT, Department of Physics, University of Antwerp, 2020 Antwerp, Belgium, [2]BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain, [3]Faculty of Applied Engineering, iPRACS, University of Antwerp, 2020 Antwerp, Belgium, [4]Ikerbasque, Basque Foundation for Science, Bilbao, 48009 Spain

matthias.quintelier@uantwerpen.be

Metal-Organic Frameworks (MOFs) have attracted significant attention for their diverse applications, particularly in gas absorption and separation. One notable application of MOF-74 is its ability to capture carbon dioxide (CO_2), which is crucial for addressing global warming [1]. However, before MOFs can be utilized, they must undergo an activation process to empty their pores and create open metal sites for gas binding.

Traditionally, the activation process has been studied using powder X-ray diffraction (PXRD) combined with other techniques such as Raman spectroscopy [2]. However, XRD is limited in this case by the small coherence length and particle size of MOFs. In the current study, for the first time, *in situ* three-dimensional electron diffraction (3DED) is used to investigate the activation process of MOF-74, specifically Cu-MOF-74 and Zn-MOF-74.

Unlike traditional techniques, 3DED and transmission electron microscopy (TEM) do not require large crystals, making them ideal for studying materials with low occupancies or periodicity at specific crystallographic positions. Our study revealed significant differences in activation behaviour between Zn-MOF-74 and Cu-MOF-74.

While heating Zn-MOF-74 to 120 °C successfully created open metal sites, heating to 350 °C did not completely empty the pores, indicating the presence of residual electrostatic potentials that could hinder gas flow during CO2 absorption. In contrast, Cu-MOF-74 exhibited rapid activation induced solely by the ultra-high vacuum of the electron microscope, attributed to the weaker Cu-O bond and greater Lewis acidity. Additionally, Cu-MOF-74 demonstrated the formation of an amorphous carbon matrix with small Cu nanoparticles after heating to 300 °C, highlighting its lower thermal stability.

These findings emphasize the importance of advanced characterization techniques like *in situ* 3DED in understanding the activation process of MOFs. By elucidating the activation dynamics of different metal-based MOFs, our study contributes to a deeper understanding of their applications and design principles. Furthermore, it showcases the potential of *in situ* 3DED as a powerful tool for advancing MOF research and applications.

[1] T. M. McDonald et al., "Cooperative insertion of CO_2 in diamine-appended metal-organic frameworks," Nature, vol. 519, no. 7543, pp. 303–308, 2015, doi: 10.1038/nature14327.

[2] X. Liang, P. Wang, C. Li, M. Yuan, Q. Shi, and J. Dong, "The activation of Co-MOF-74 with open metal sites and their corresponding CO/N_2 adsorptive separation performance," Microporous Mesoporous Mater., vol. 320, Jun. 2021, doi: 10.1016/j.micromeso.2021.111109.